

Copper-Indium-Boron-Diselenide Absorber Materials

Natale J. Ianno¹, Rodney J. Soukup¹, Tobin Santero¹, Chad Kamler¹, James Huguenin-Love¹, Scott A. Darveau², Jiri Olejnicek², and Christopher L. Exstrom²

¹Dept. of Elec. Eng., University of Nebraska-Lincoln, 209N WSEC, Lincoln, NE, 68588-0511

²Dept. of Chemistry, University of Nebraska at Kearney, 905 West 25th Street, Kearney, NE, 68849-1150

ABSTRACT

Attempts to fabricate new $\text{CuIn}_{1-x}\text{B}_x\text{Se}_2$ (CIBS) and CuBSe_2 (CBS) thin-film materials have been complicated by the formation of interfering crystallites and by the loss of boron from the magnetron sputtered precursor alloys during the selenization and annealing processes. Raman and Auger spectroscopic analysis as well as X-ray diffraction studies show that the formation of boron selenide may be contributing to the difficulty in creating these new materials.

INTRODUCTION

While much progress has been made in photovoltaic cell development, the United States still does not have a cost-competitive version of a solar cell for domestic or industrial applications except in very remote areas of the country. In order for photovoltaic systems to be competitive, a 15% module efficiency with an installed efficiency of 12% at a cost of \$1/Wp and a 20 year lifetime must be achieved. Broad-based U.S. government-supported research has determined that this goal can most likely be met by thin-film solar cells [1]. Of these thin film materials, the CuInSe_2 (CIS) family shows the most promise [2]. Unfortunately, solar cells produced with CIS as the absorber layer are limited in efficiency as a consequence of the relatively small bandgap of 1.04 eV [3]. Ongoing research has been directed toward materials for which lighter elements from group IIIA of the periodic table are substituted in part for the indium in order to increase the bandgap.

To date, the greatest energy conversion efficiency, 19.5%, has been achieved with a $\text{CuIn}_{0.74}\text{Ga}_{0.26}\text{Se}_2$ (CIGS) absorber layer which has a bandgap of 1.15 eV with an open circuit output voltage of 0.701 V [4,5]. Changes in the bandgap structure limits the maximum amount of Ga that can be substituted and still allow the solar cell to maintain this higher efficiency.

We are working toward the fabrication and study of a new material, copper indium boron diselenide, $\text{CuIn}_{1-x}\text{B}_x\text{Se}_2$ (CIBS), which, to the best of our knowledge, has never been grown and studied. Boron should yield a higher bandgap, closer to the ideal value of 1.5 eV, for lower concentrations of boron than either gallium or aluminum [6]. We anticipate this lower concentration to lead to thin ordered films approaching the idealized chalcopyrite crystal structure of CIS. This material has not been studied because the excessively high boiling point of boron prevents its deposition by evaporation, the classical means of producing CIS-based solar cell films.

Boron concentration in the films is a critical parameter in projecting what bandgaps may be achieved. Based on the results for Ga and Al substitution, [6] we have calculated that less than 24% boron will result in a bandgap near 1.5 eV. To estimate this, the bandgaps of CuInSe_2 , CuGaSe_2 , and CuAlSe_2 were plotted as a function of the atomic mass of the column III elements

and a perfect logarithmic fit was found, see figure 1. This curve was then extrapolated to the atomic mass of B and yielded an estimated bandgap for CuBSe₂ of E_g = 3.16eV. Equation (1) in the paper by Wei and Zunger [6] is repeated here

$$E_g(x) = (1-x) E_g(A) + x E_g(B) -bx(1-x) \quad (1)$$

where A is indium and, in our case, B is boron and x is the fraction of boron concentration. This equation was then used to determine x, the fraction of B to be used. Given that reported b values for Cu(Al,Ga)Se₂ and Cu(Ga,In)Se₂ range from -0.07 to 0.28[6], b values between -0.1 and 0.4 were applied in our calculation to yield an x value range of 21-25 at. % for a CIBS film to have a bandgap near 1.5 eV. Thus, the concentration required to achieve a given band gap is not strongly dependent on the parameter b. This percentage is comparable to the Ga-substitution percentage in CIGS which yields the highest efficiency solar cell to date [3]. Thus, it appears feasible that a CIBS film with chalcopyrite structure integrity can be fabricated.

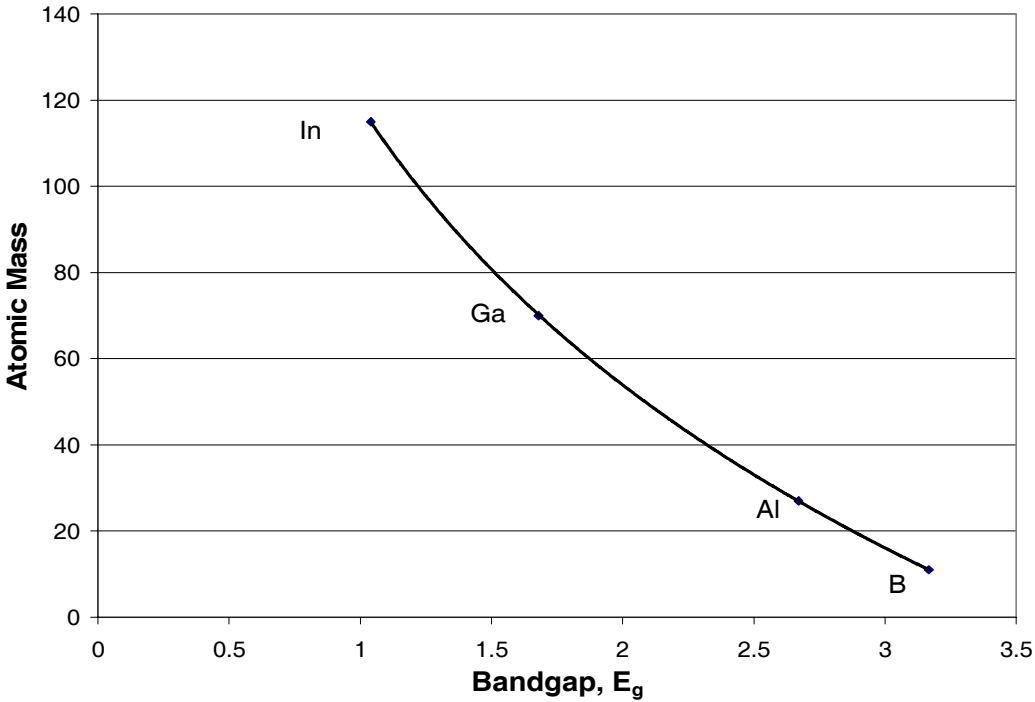


Figure 1. Approximate bandgaps of CuXSe₂ (X = B, Al, Ga, In) as a function of the atomic mass of X. Values for CuAlSe₂, CuGaSe₂, and CuInSe₂ bandgaps are from ref. 6. The trend is extrapolated to estimate the CuBSe₂ bandgap.

EXPERIMENT

The copper-indium and copper-indium-boron precursor films were co-sputtered in an AJA International ATC 1600 Sputtering System that routinely reaches a base pressure of approximately 1×10^{-4} Pascal. The argon sputtering gas is directly injected between the target and ground shield of each planar magnetron sputter gun, at a flow rate of 15 sccm into each gun. The

substrates were loaded into the chamber through a load lock onto the rotating, heated substrate holder.

The copper and indium guns were driven by dc power supplies, while the boron gun was driven by an rf supply. The precursor samples, all between 400 and 600nm thick, were analyzed by Auger Depth Profiling to determine their composition and uniformity. All samples were selenized in a quartz halogen lamp heating system using a solid, pure selenium source. The selenium was placed in a graphite boat along with the substrate. The boat was loaded into a quartz tube which was evacuated by a mechanical pump to a base pressure of less than 1 Pascal. A thermocouple is embedded into the boat and serves as the process temperature monitor. A two step ramp and soak process was employed where a 10 minute ramp to 250 °C followed by a 20 minute soak were followed by another 10 minute ramp to the selenization temperature and another 20 minute soak. A controlled cool down returned the boat to room temperature [7].

Selenized samples were characterized by θ -2 θ X-ray diffractometry, Raman Spectroscopy and Auger Depth Profiling.

RESULTS AND DISCUSSION

A comparison of XRD spectra for precursor Cu_xIn_y , $\text{Cu}_x\text{In}_y\text{B}_z$ and Cu_xB_z films showed that boron had virtually no effect on the observed Cu_2In and $\text{Cu}_9\text{In}_{11}$ peaks. The XRD spectra for the selenized precursors are seen in figure 2. Peaks consistent with CIS-type structure are apparent for both selenized Cu_xIn_y and $\text{Cu}_x\text{In}_y\text{B}_z$ films. Results from the selenized Cu_xB_z film are most consistent with several Cu_{2-x}Se phases.

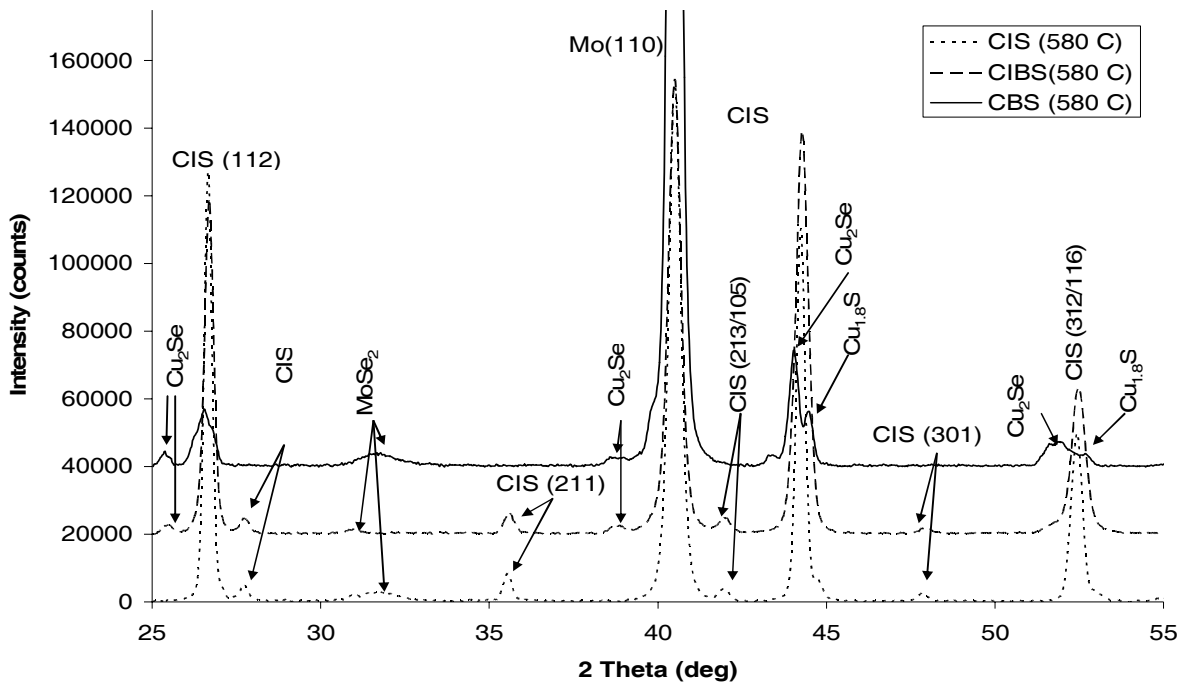


Figure 2. X-ray diffraction scans of CIS, CIBS and CBS films. The intensity of the CIBS and CBS films are offset for clarity.

The expected shift in the CIS (112) peak for the selenized $\text{Cu}_x\text{In}_y\text{B}_z$ film as a result of substituting the smaller boron atom for the indium is not apparent and any small shift may be more consistent with mixed CIS and $\text{Cu}_{1.8}\text{Se}$ phases [8-10].

Raman Spectra of the same Cu_xIn_y , $\text{Cu}_x\text{In}_y\text{B}_z$ and Cu_xB_z films following selenization at 580°C are seen in figure 3. Note the presence of CuInSe_2 signals from the selenized Cu_xIn_y and $\text{Cu}_x\text{In}_y\text{B}_z$ films and the lack of a signal near $170 - 190 \text{ cm}^{-1}$ for the selenized Cu_xB_z film.

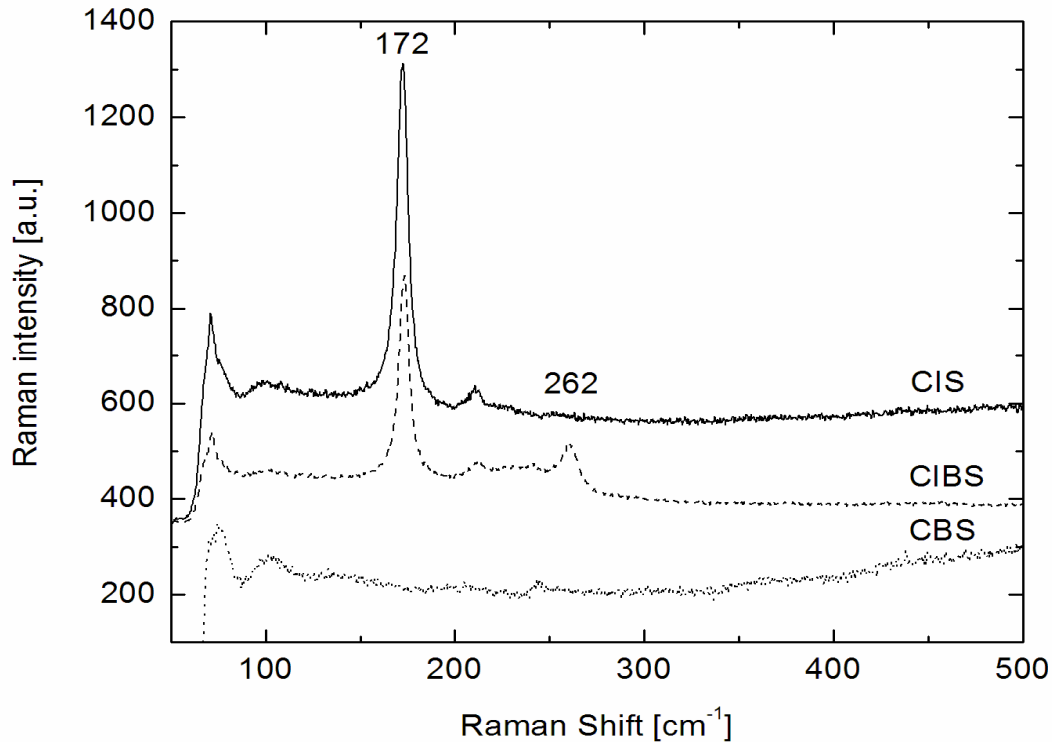


Figure 3. Raman spectrum of Cu_xIn_y , $\text{Cu}_x\text{In}_y\text{B}_z$ and Cu_xB_z films following selenization at 580°C

Optical microscope images of selenized $\text{Cu}_x\text{In}_y\text{B}_z$ films revealed isolated surface crystallites with apparently distinct morphologies. When the incident laser beam was focused on these crystallites, the Raman spectra seen in Fig. 4 included a peak near 840 cm^{-1} that is consistent with the presence of B_2Se_3 [11]. Portions of the films outside these crystallites gave Raman spectra with no peak at 840 cm^{-1} but otherwise identical to figure 4. The resulting conclusion is that B remains in the film in isolated regions, rather than throughout the entire film.

Figure 5 shows an Auger depth profile of a selenized $\text{Cu}_x\text{In}_y\text{B}_z$ film. An Auger depth profile was run on the film prior to selenization. The results indicated that copper, indium and boron were uniform throughout the film. Sputter deposition of this film was accomplished using a 45%Cu-55%In target, a second pure Cu target and a B target. The precursor film contained about 57% copper, 28% boron and 15% indium. A look at the analysis presented in figure 5 illustrates that the elements are no longer uniformly distributed after selenization, but that the boron accumulates at the bottom of the film while copper and selenium decrease in relative

concentration as a function of depth into the film. The indium signal appears to peak near the center of the film. In order to confirm that this was not a result of the selenization process, numerous copper indium precursors selenized and depth profiled and showed uniform distribution of the elements through the thickness of the film.

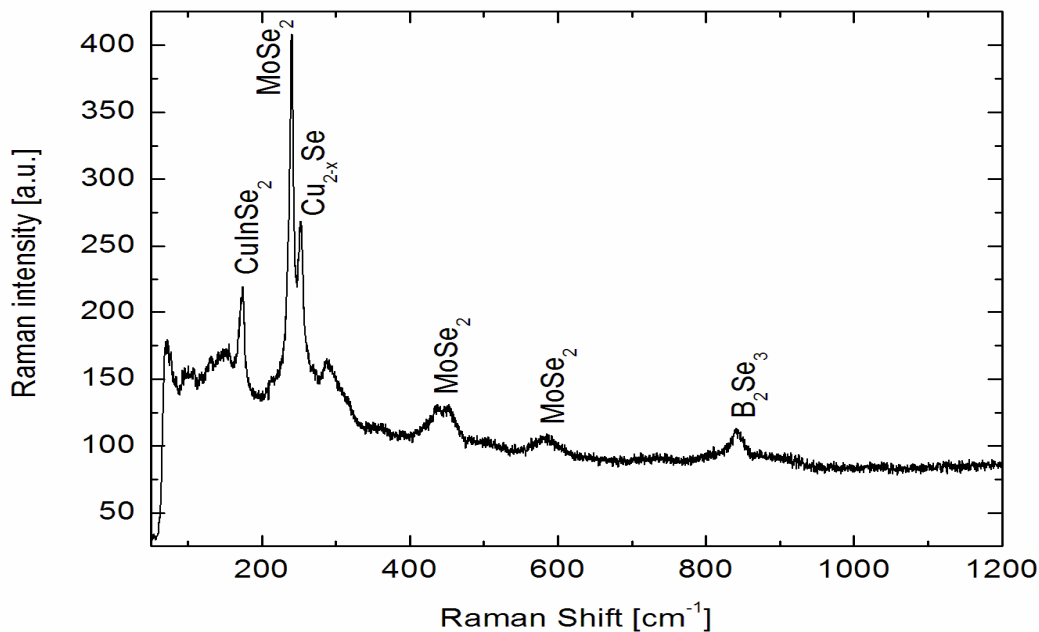


Figure 4. Raman Spectra of a crystallite on the surface of a selenized copper-indium-boron film and the surrounding area.

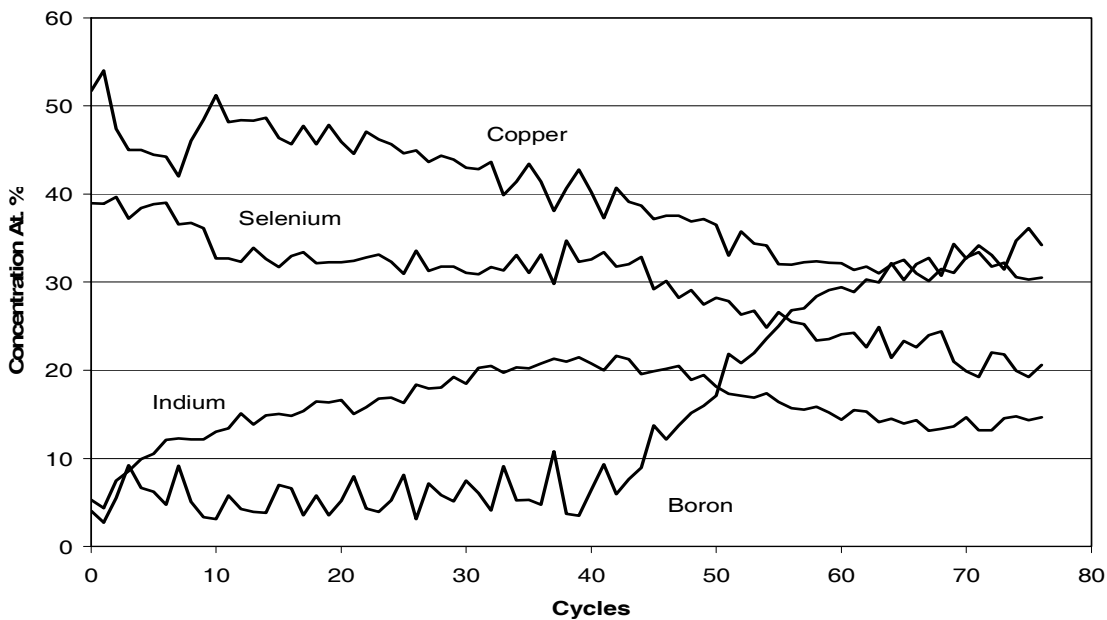


Figure 5. Auger depth profile of a selenized copper-indium-boron film.

CONCLUSIONS

The magnetron sputtering system is capable of introducing boron into a CuIn metal alloy. However, the selenization and annealing processes appear to result in either the loss of boron entirely or the formation of an undesirable B_2Se_3 phase atop a $CuInSe_2$ or $Cu_{2-x}Se$ layer. The remaining boron appears to accumulate near the film-substrate interface. A similar result for aluminum was observed for selenized $CuIn_{1-x}Al_x$ precursors.[12]

Future experiments are needed in order to optimize the selenization and annealing processes to overcome the boron selenide formation, boron loss, and boron segregation problem. One potential approach may be to allow the formation of the boron selenide followed by the deposition of a Cu(In) overlayer that upon annealing may trap the boron and force the formation of $CuIn_{1-x}B_xSe_2$ or $CuBSe_2$. These new experiments are being carried out.

ACKNOWLEDGMENTS

The authors would like to acknowledge the work of our students: T. Haussler, T. Brown, A. Martinez-Skinner, A. Vandeventer, M. Ingersoll, A. Mirasano, and A. Wegener.

We acknowledge the support of the U.S. Department of Energy, contract number DE-FG02-06ER64235 and the support of the Nebraska Research Initiative.

REFERENCES

1. R.J. Soukup, *Jemná Mechanika a Optika* **1**, 12 (1995).
2. R. Noufi, K. Zweibel in *Proceedings 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion*, (Institute of Electrical and Electronics Engineers, Inc. (IEEE) Vol. 1: Piscataway, NJ 2006) pp. 317-320.
3. K. Ramanathan, G. Teeter, J.C. Keane and R. Noufi, *Thin Solid Films* **480-481**, 499 (2005).
4. M.A. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D.L. Young, B. Egaas and R. Noufi, *Progress in Photovoltaics: Research and Applications* **13**, 209 (2005).
5. J.T. Heath, J.D. Cohen and W.N. Shafarman in *Compound Semiconductor Photovoltaics*, edited by R.Noufi, W. N. Shafarman, D. Cahen, and L. Stolt, (Mat. Res. Soc. Symp. Proc. **763** Pittsburgh, PA, 2003) pp. B9.2.1-B9.2.6.
6. S.-H. Wei and A. Zunger, *J. Appl. Phys.* **78**, 3846 (1995).
7. F. Adurodija, J. Song, S.K. Kim, Ki.H.Kang, K.H. Yoon, S.H. Kwon, B.T. Ahn, and S.D. Kim, *Journal of the Korean Physical Society* **32**, 87 (1998).
8. W. Gebicki, M. Igalson, W. Zajac, and R. Trykozko, *Journal of Physics D: Applied Physics* **23**, 964 (1990).
9. Y.B.K. Reddy, V.S. Raja, and B. Sreedhar, *Journal of Physics D: Applied Physics* **39**, 5124 (2006).
10. D.K. Suri, K.C. Nagpal, and G.K. Chadha, *Journal of Applied Crystallography* **22**, 578 (1989).
11. R. Hillel, and J. Cueilleron, *Bulletin De Laq Société Chimique de France* **1**, 98, (1972).
12. J.H. Yun, R.B.V. Chalapathy, J.C. Lee, J. Song, and K.H. Yoon, *Solid State Phenomena* **124-126**, 975 (2007).